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High-resolution photoemission study of $CeRu_2$: The dual character of 4*f* electrons

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High-resolution low-temperature photoemission spectroscopy was performed for $CeRu_2$ to study the nature of low-lying excitations around the Fermi level (E_F). It was found that the photoemission spectrum near E_F shows two well-resolved peaks at and about 270 meV below E_F, which are ascribed to the tail of the Ce 4 f^1 final state located just above E_F and its spin-orbit satellite ($\Delta_{SO} \sim 270$ meV), respectively. This suggests that the many-body-correlation effect is necessary for understanding the electronic structure near E_F of $CeRu_2$, although the Ce 4*f* electron exhibits a substantially itinerant character through the strong hybridization with the conduction electrons. [S0163-1829(96)50322-X]

$CeRu_2$ shows superconductivity with a relatively high transition temperature T_c of about 6.1 K and has been a subject of intensive attention due to its unique electronic and magnetic properties in relation to the mechanism of the superconductivity.[1] It had been thought that a Ce atom in $CeRu_2$ is tetravalent with no 4*f* electrons ($4f^0$) and consequently the superconductivity is associated with only the Ru sublattice and its *d* electrons. In contrast with this simple view of the electronic structure, electron-spectroscopic studies[2–5] have suggested that $CeRu_2$ is a mixed valent with a substantial weight of the $4f^1$ configuration. Meanwhile, using the self-consistent augmented plane wave method, Yanase has shown that $CeRu_2$ has an appreciably wide 4*f* band with the *f* electron count being close to one.[6] These remind us of a possible similarity to the well-known heavy-fermion superconductor $CeCu_2Si_2$.[7] Of course, there is much experimental evidence that $CeRu_2$ has a strong itinerant character, such as the small electronic specific heat coefficient,[8] the paramagnetic behavior,[9] and the de Haas–van Alphen measurement.[10] However, it is also true that there are substantial deviations from a simple one-electron picture, such as the superconducting parameters different from conventional BCS values.[8] These conflicting experimental results seem to suggest a strong hybridization of Ce 4*f* electrons with the conduction band and a resultant dual character (itinerant and localized) of the Ce 4*f* electrons in $CeRu_2$.

We have carried out a high-resolution low-temperature photoemission measurement on $CeRu_2$ to study the detailed electronic structure near the Fermi level (E_F), which directly relates to the low-lying excitations and superconductivity. Recent progress in improving the energy resolution in photoemission spectroscopy has enabled a remarkably precise analysis of the electronic structure near E_F, in particular, of strongly correlated electron systems such as oxide superconductors and heavy-fermion materials. High-resolution photoemission spectroscopy (HRPES) of various cerium compounds has established the existence of a very narrow peak at E_F with some additional satellites.[11,12] The E_F peak and the satellites have been ascribed to the Kondo-resonance peak and the spin-orbit and crystal-field splitting satellites, respectively, while there is still a hot debate on the origin.[13–15] We found in this study that the HRPES spectrum of $CeRu_2$ exhibits two peaks near E_F ascribable to the Kondo peak and the spin-orbit satellite in a very similar manner to other cerium compounds, in contrast with the reported substantial itinerant character of $CeRu_2$. This suggests a dual character (itinerant and localized) of the Ce 4*f* electrons in $CeRu_2$ as well as a strong hybridization between the Ce 4*f* electrons and the conduction band.

A single crystal of $CeRu_2$ was prepared by argon arc melting of high-purity metals. The structure and single crystallinity were checked by x-ray diffraction, which showed the Laves phase (C15) pattern with a lattice constant of about 7.5 Å as reported previously.[8] Photoemission measurements were carried out with a homemade high-resolution photoemission spectrometer which has a large hemispherical electron analyzer (diameter, 300 mm) and a highly bright discharge lamp. The base pressure is 2×10^{-11} Torr and the energy resolution was set at 35/40 meV for He I (21.2 eV)/ He II (40.8 eV) measurements. The working pressure during the lamp operation was 5×10^{-10}–1×10^{-9} Torr. The $CeRu_2$ single crystal was scraped *in situ* by a diamond file just before photoemission measurements to obtain a clean and fresh surface. All the procedures (scraping and measurement) were done by keeping the sample at 15 K. Since we observed degradation of the sample surface as being evident by a gradual growth of an additional feature at 10 eV binding energy in the photoemission spectrum after an hour,[16] we repeated scraping every 5 min and obtained a final spectrum with a good signal-to-noise ratio by adding each scan. The Fermi level of the sample was referenced to that of a gold

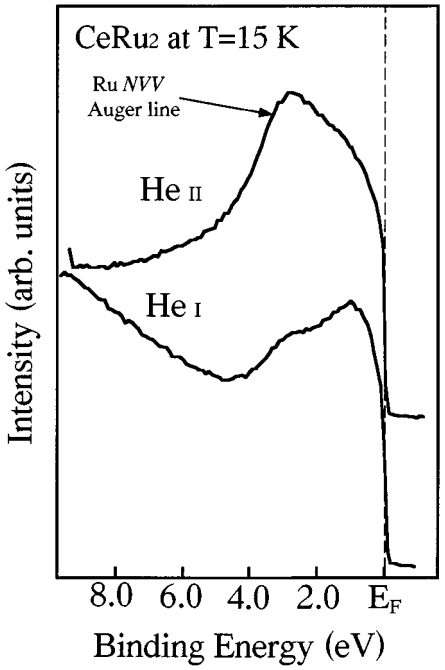

FIG. 1. Valence-band photoemission spectra of $CeRu_2$ measured at 15 K with the He I (21.2 eV) and He II (40.8 eV) resonance lines.

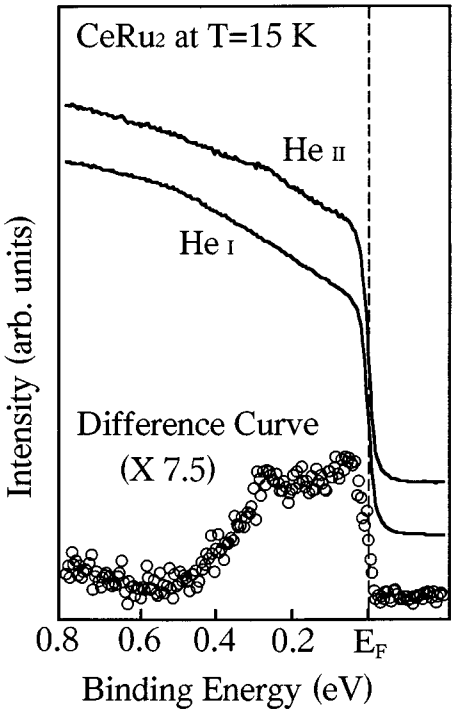

FIG. 2. High-resolution photoemission spectra near E_F of $CeRu_2$ measured at 15 K with the He I and He II resonance lines, together with the difference curve obtained by subtracting the He I spectrum from the He II.

film deposited on the sample substrate and its position was accurate to better than 2 meV.

Figure 1 shows the valence band photoemission spectra of $CeRu_2$ measured with the He I and He II resonance lines at 15 K. We find two broad features at about 1 and 3 eV in the He I spectrum. Since the photoionization cross section of the Ru 4*d* orbital is substantially large in the He I excitation compared with other orbitals, these two features represent mostly the Ru 4*d* bands, while a Ce $4f^0$ peak is expected to contribute to the feature around 3 eV. The observed close proximity of the Ru 4*d* density of states to E_F shows a good agreement with the band-structure calculation,[6] indicating the strong hybridization between the Ru 4*d* band and the Ce 4*f* states. When we compare the He I spectrum with the He II, we notice a large enhancement of a broad peak around 3 eV. This enhancement of the 3-eV band is due to the Ru *NVV* Auger since the He II photon energy almost coincides with the Ru 4*p*-4*d* excitation (about 40 eV).[17]

Figure 2 shows the He I and He II photoemission spectra of $CeRu_2$ in the vicinity of E_F. Although both spectra look very similar to each other, we find two small structures at and about 0.3 eV below E_F in the He II spectrum. This becomes clearer in the difference curve obtained by subtracting the He I spectrum from the He II (Fig. 2). Since the ratio of the photoionization cross section of the He II photon to the He I for the Ce 4*f* orbital is considerably large compared with other orbitals,[18] the difference curve represents mostly the Ce 4*f* derived states. In the subtraction procedure, the intensity of the spectrum is normalized at 0.6 eV binding energy since both spectra become almost parallel around this binding energy.[19] A slight upturn of the difference curve in the higher binding energy region (0.7~0.8 eV) may be due to a tail of the Ru *NVV* Auger peak around 3 eV binding energy. The two-peaked structure in the near-E_F photoemission spectrum as in Fig. 2 has also been observed in many other cerium compounds;[20] the E_F peak has been explained as the Ce $4f^1$ final state ($4f^1_{5/2}$), namely a tail of the Kondo resonance peak produced by the Kondo-type screening of the localized *f* state by the conduction electrons, while the 270-meV peak has been ascribed to the spin-orbit satellite ($4f^1_{7/2}$). Whereas the single-ion Kondo model based on the Anderson Hamiltonian[21] has well explained the photoemission spectrum and its Kondo-temperature (T_K) dependence in some cerium compounds such as $CeSi_x$,[22] it also appears to have a limitation in highly mixed systems with a high T_K such as $CeNiSi_2$.[23] In fact, when we carried out a noncrossing-approximation (NCA) calculation[21] based on the single-ion Kondo model for $CeRu_2$ using reasonable parameters estimated from the Kondo temperature (~1000 K),[9] we could not reproduce the difference curve in Fig. 2 since the calculated spectrum showed a very sharp and enhanced Kondo peak at E_F in contrast with the obtained difference curve. One can claim that the suppression and smear-out of $4f^1_{5/2}$ peak may be ascribed to the surface effects. According to the previous study of the surface effect in cerium compounds,[15] the surface of cerium compounds has a stronger γ-Ce-like character, i.e., more localized *f* states and resultantly leads to show a relatively weak $f^1_{5/2}$ peak. However a comparative high-resolution PES study for α Ce and γ Ce (Ref. 20) under almost the same experimental condition as ours shows that the spectrum of $CeRu_2$ is very similar to that of γ Ce but not to that of α Ce. Since a surface effect would be almost the same between the present and the previous measurements,[20] the similarity of the photoemission spectrum implies that Ce 4*f* electrons in $CeRu_2$ have a substantial localized nature like in γ Ce which exhibits an archetypical Curie-Weiss behavior.[24] All these suggest the single-

impurity Anderson model has a limitation in highly hybrided systems like $CeRu_2$ while the electronic structure near E_F cannot be fully described within the one-electron band scheme.

In conclusion, we found that the 4*f*-derived high-resolution photoemission spectrum near E_F of $CeRu_2$ exhibits two peaks at and about 270 meV below E_F. The E_F and 270-meV peaks are ascribed to the Kondo peak ($4f^1_{5/2}$ final state) and the spin-orbit satellite ($4f^1_{7/2}$), respectively, as in other cerium compounds, although the NCA calculation based on the single-ion Kondo model using parameters estimated from the Kondo temperature cannot reproduce quantitatively the spectrum. This indicates a dual character (itinerant and localized) of 4*f* electrons in $CeRu_2$ as well as a limitation of the NCA calculation for a high-T_K cerium compound such as $CeRu_2$.

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[1] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Lett. **1**, 449 (1958).
[2] J. C. Fuggle, F. U. Hillebrecht, Z. Zolinerek, and R. Lasser, Phys. Rev. B **27**, 7330 (1983).
[3] J. W. Allen, S.-J. Oh, I. Lindau, M. B. Maple, J. F. Suassuna, and S. B. Hagström, Phys. Rev. B **26**, 445 (1982).
[4] J. W. Allen , S.-J. Oh, M. B. Maple, and M. S. Torikachvili, Phys. Rev. B **28**, 5347 (1983).
[5] M. Croft, R. Neifeld, B. Qi, G. Liang, D. Perez, and S. Gunapala, in *Valence Fluctuations and Heavy Fermions*, edited by L. C. Gupta and S. K. Malik (Plenum, New York, 1987), p. 217.
[6] A. Yanase, J. Phys. F **16**, 1501 (1986).
[7] R. D. Parks, B. Reihl, N. Martensson, and F. Steglich, Phys. Rev. B **27**, 6052 (1983).
[8] R. R. Joseph, K. A. Gschneider, Jr., and D. C. Koskimaki, Phys. Rev. B **6**, 3286 (1972).
[9] F. E. Brown, J. E. Hebborn, and P. S. Scenes, J. Phys. F **1**, 903 (1971).
[10] H. Sugawara (private communication).
[11] F. Patthey, W.-D. Schneider, Y. Baer, and B. Delley, Phys. Rev. B **34**, 2967 (1986).
[12] T. Takahashi, T. Morimoto, T. Yokoya, S. Kunii, T. Komatsubara, and O. Sakai, Phys. Rev. B **52**, 9140 (1995).
[13] J. J. Joyce, A. J. Arko, J. M. Lawrence, P. C. Canfield, Z. Fisk, R. J. Barlett, and J. D. Thompson, Phys. Rev. Lett. **68**, 236 (1992).
[14] D. Malterre, M. Grioni, P. Weibel, and Y. Baer, Phys. Rev. Lett. **68**, 2656 (1992).
[15] E. Weschke, C. Laubshat, R. Ecker, A. Höhr, M. Domke, and G. Kaindl, Phys. Rev. Lett. **69**, 1792 (1992).
[16] This feature around 10 eV may be due to residual gases such as N_2 and CO condensed on the cold sample surface.
[17] *Photoemission in Solids II*, edited by L. Ley and M. Cardona (Springer-Verlag, Berlin, 1979), p. 378.
[18] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).
[19] We have tried several subtractions with different normalizing points at 0.4–1.0 eV. In every case, a two-peaked structure as in Fig. 2 appears in the subtracted spectrum, although the intensity around 0.6 eV becomes negative after subtraction when we normalize the intensity at a point away from 0.6 eV.
[20] F. Patthey, J.-M. Imer, W.-D. Schneider, H. Beck, Y. Baer, and B. Delley, Phys. Rev. B **42**, 8864 (1990).
[21] N. E. Bickers, D. L. Cox, and J. W. Wilkins, Phys. Rev. B **36**, 2036 (1987).
[22] T. Takahashi, T. Morimoto, T. Yokoya, M. Kohgi, and T. Satoh, Phys. Rev. B **49**, 15 688 (1994).
[23] H. Kumigashira, A. Chainani, T. Yokoya, O. Akaki, T. Takahashi, M. Ito, M. Kasaya, and O. Sakai, Phys. Rev. B **53**, 2565 (1996).
[24] P. Burgardt, K. A. Gschneidner, Jr., D. C. Koskenmaki, D. K. Finnermore, J. O. Moorman, S. Legvold, C. Stassis, and T. A. Vyrostek, Phys. Rev. B **14**, 2995 (1976).